Supramolecular Silanol Chemistry: Inclusion Complexes of 1,3,5-Tris(diisopropylhydroxysilyl)benzene and 4,4'-Bis(pyridines)

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The trisilanol 1,3,5-(HO*i*Pr₂Si)₃C₆H₃ (**5**), a novel building block for applications in supramolecular chemistry, has been prepared via the intermediates 1,3,5-(H*i*Pr₂Si)₃C₆H₃ (**6**) and (Cl*i*Pr₂Si)₃C₆H₃ (**7**). The inclusion complexes **5**·0.5H₂O, **5**·bpy·0.5H₂O, **5**·bpe, **5**·azpy and **5**·bpa have been investigated by X-ray crystallography [bpy = 4,4'-bipyridine, bpe = (*E*)-bis(4-pyridyl)ethylene, azpy = 4,4'-azopyridine, bpa = bis(4-pyridyl)aceylene]. The ratio between donor and acceptor molecules is always 1:1 and the crude supramolecular motifs are very similar for **5**·bpy·0.5H₂O, **5**·bpe, **5**·azpy and **5**·bpa. The trisilanol molecules form 1D chains, which are

connected by nearly perpendicular 4,4'-bis(pyridine) molecules to give rise to formation of 2D grid networks featuring O–H···O(H)Si and O–H···N hydrogen bonds. Differences are observed in the shape and size of the voids defined by the 2D grids. The smaller voids are blocked by trisilanol molecules of adjacent 2D networks in case of $5\cdot$ bpy·0.5H₂O and $5\cdot$ bpe. In case of $5\cdot$ azpy, the larger voids are filled by interpenetration of the same 2D networks.

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Introduction

Organosilanols are well known for their extensive selforganisation in the solid state, which has led to the observation of a great variety of different hydrogen-bond patterns.^[1] In most cases organosilanols form hydrogen bonds with themselves, but occasionally co-crystals with alcohols,^[2] ethers^[3] and amines^[4] have been observed. Whilst the majority of these complexes has been formed inadvertently with solvent and reagent molecules, recently a small number of inclusion complexes has been prepared deliberately by co-crystallisation studies.^[5] However, the vast potential of organosilanols in molecular recognition has not yet been exploited for applications in supramolecular chemistry and crystal engineering. The organosilanols used in previous studies lack topological pre-organisation of the silanol sites on a molecular level, a prerequisite for genuine control of supramolecular structures.

Gaining control over solid-state structures requires the judicious choice of molecular building blocks ("synthons") possessing adhesive functional groups ("tectons") with prefixed directionality.^[6] 1,3,5-Trimesic acid, 1,3,5-(HOOC)₃- C_6H_3 (1), the prime building block for organic supramolecular chemistry fulfils this criterion and gives rise to formation of honeycomb ("chicken-wire") networks containing nano-dimensional cavities in the solid state, which may be useful for applications in host–guest chemistry (Scheme 1).^[7] Organometallic chemistry can extend the range of useful building blocks for supramolecular chemistry by a wealth of adhesive functional groups.^[8] For in-



Scheme 1.

[a] Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34–36, 14195 Berlin, Germany stance, 1,3,5-benzenetriphosphonic acid, $1,3,5-(H_2O_3P)_3-C_6H_3$ (2), has been used for co-crystallisation studies with



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a number of amines, which has given rise to formation of inclusion complexes revealing N–H \cdots OP hydrogen-bond contacts (Scheme 1).^[9]

Recently, we have prepared 1,3,5-(hydroxydiorganosilyl)benzenes, 1,3,5-(HOR₂Si)₃C₆H₃ (**3**, R = Me; **4**, R = Ph) and investigated their supramolecular structures (Scheme 1).^[10] Unfortunately, all attempts to prepare inclusions complexes of 1,3,5-(hydroxydiorganosilyl)benzenes and amines have not yet been successful. In case of 3, the amines have basecatalysed the condensation and formation of siloxanes, whereas in case of 4, C–H··· π stacking is presumably the predominant crystal-packing force, precluding the formation of inclusion complexes with amines.^[11] We have now prepared a novel 1,3,5-(hydroxydiorganosilyl)benzene, $1,3,5-(HOiPr_2Si)_3C_6H_3$ (5) possessing bulky and aliphatic isopropyl groups, which are able to circumvent the difficulties encountered with 3 and 4 in co-crystallisation studies with amines. Herein, we describe co-crystals of 5 with 4,4'bipyridine (bpy), (E)-bis(4-pyridyl)ethylene (bpe), 4,4'-azopyridine (azpy) and bis(4-pyridyl)aceylene (bpa) that exhibit similar supramolecular motifs featuring 2D grid networks of O-H···O(H)Si and O-H···N hydrogen bonds.

Results and Discussion

The synthesis of the trisilanol 1,3,5-(HO*i*Pr₂Si)₃C₆H₃ (**5**) has been achieved in three steps starting from commercially available 1,3,5-tribromobenzene (Scheme 2). The diisopropylsilyl groups have been introduced by the in situ Grignard reaction of 1,3,5-Br₃C₆H₃ with *i*Pr₂SiHCl/Mg affording 1,3,5-(H*i*Pr₂)₃C₆H₃ (**6**) as a distillable oil. Chlorination of **6** using SO₂Cl₂ has provided the corresponding chlorosilane 1,3,5-(Cl*i*Pr₂)₃C₆H₃ (**7**) as distillable oil that solidifies upon standing at room temperature. The base hydrolysis of **7** pro-

vides the trisilanol 1,3,5-(HO*i*Pr₂Si)₃C₆H₃ (**5**) as a low-melting crystalline solid.

Solid-State Structure of 5

After recrystallisation from CH₂Cl₂/hexane, the trisilanol $1,3,5-(HOiPr_2Si)_3C_6H_3$ (5) has been obtained free of crystal water. The IR spectrum (KBr pellet) of this material exhibits two absorptions at 3694 cm⁻¹ (sharp, intense) and 3345 cm⁻¹ (broad, very intense), which were assigned to stretching vibrations of hydroxy groups that are free and involved in hydrogen bonding, respectively.^[12] This assignment is supported by a preliminary X-ray structure analysis,^[13] which reveals that only one silanol group is engaged in hydrogen bonding, whereas the other two are free. Unfortunately, severe disorder or twining has precluded the satisfying refinement of the X-ray data. When slowly crystallised from toluene the trisilanol was isolated as a hemihydrate, 5.0.5H₂O, which has been investigated by X-ray diffraction. A perspective view of the supramolecular structure of 5.0.5H₂O is shown in Figure 1. Crystal and refinement data are collected in Table 6. The asymmetric unit contains three crystallographically independent molecules of 5 (denoted A, B and C) and water. Twelve O…O distances between 2.684(3) and 2.871(3) Å are indicative for weak to medium-strength hydrogen bonding and are listed in Table 1. The exact donor-acceptor relationship could not be established from the erratic refinement of the hydrogen positions. However, from the close proximity of the water molecules (O11-O12) to four oxygen atoms of the silanol groups it can be deduced that each water molecule serves twice as donor and acceptor for a total of four hydrogen bonds. The supramolecular motif around the water molecules can be described best as a spirocyclic arrangement of two eight-membered rings each consisting of four oxygen



Scheme 2.



Figure 1. Perspective view of the inclusion complex 5.0.5H₂O (only SiO groups of the outer trisilanol molecules are shown for clarity).

and four hydrogen atoms. The eight-membered rings feature one water molecule and three silanol groups and therefore somewhat resemble the hydrogen-bond motif observed for the hydrate of 4.^[10] The participation of all silanol groups in hydrogen bonding is confirmed by an IR spectrum (KBr) of 5·0.5H₂O, which shows one absorption at 3357 cm⁻¹ (broad, very intense).

Table 1. Donor acceptor distances [Å] of the hydrogen bonds of $5{\cdot}0.5{\rm H}_2{\rm O}.$

O–H···O(H)Si		O–H···OH ₂	
0103	2.719(2)	O2…O11	2.757(5)
01…04	2.778(2)	O3…O10	2.761(3)
0209	2.700(3)	O4…O10	2.791(5)
05…06	2.739(3)	O6…O12	2.861(3)
O5…O7	2.675(3)	O7…O12	2.809(5)
O8…O9	2.771(3)	O8…O11	2.783(3)

Inclusion Complexes of 5 with 4,4'-Bis(pyridines)

Co-crystals of **5** with 4,4'-bipyrdine (bpy), (*E*)-bis(4-pyridyl)ethylene (bpe), 4,4'-azopyridine (azpy) and bis(4-pyridyl)acetylene (bpa) have been obtained and investigated by X-ray crystallography. Crystal and refinement data are collected in Table 6. To account for the fact that the trisilanol **5** and the 4,4'-bis(pyridines) contain three potential H-donors sites and two potential H-acceptor sites, respectively, the ratio of the reactants was originally intended to be 2:3. However, all isolated co-crystals consist of equimolar amounts of the trisilanol **5** and the acceptor molecule, which has been confirmed by microanalyses and ¹H NMR spectroscopy. The same co-crystals are also formed when an excess of the trisilanol **5** is used.

A perspective view of the inclusion complex 5.bpy.0.5H₂O is shown in Figure 2. Hydrogen-bond parameters are collected in Table 2. The asymmetric unit contains two crystallographically independent molecules of 5 (denoted as A and B) and bpy as well as one water molecule, which are associated through hydrogen bonding. The donor-acceptor relationship has been unambiguously established by complete refinement of all relevant hydrogen atoms. The trisilanol molecules are linked by hydrogen bonds (O3-H3···O4/O6-H6···O1) into 1D chains, in which the benzene rings are nearly coplanar. These 1D chains are connected by two bpy pillars and one water molecule giving rise to the formation of a 2D grid structure. The connection between the 1D chains and the bpy pillars is realised by two hydrogen-bond junctions (O1-H1···N1/O7-H7A···N2/ O2-H···O7 and O4-H4···N3/O5-H5···N4) running approximately in parallel. This 2D grid network is linked to adjacent networks by an additional hydrogen bond (O7-H7B····O5) being associated with the water molecule. Adjacent network layers are aligned parallel without penetration and are shifted with respect to each other by half length of the supramolecular repeating unit, so that the 1D chains are situated in close proximity to the bpy pillars of the adjacent layers. This crystal packing avoids larger cavities in the lattice

A perspective view of the inclusion complex 5-bpe is shown in Figure 3. Hydrogen-bond parameters are collected in Table 3. The asymmetric unit contains only one molecule of 5 and one bpe molecule, which are linked by hydrogen bonding. The position of all relevant hydrogen atoms has been located during the X-ray data refinement. The supramolecular motif can be described best as 2D brick-wall structure. Therein, the trisilanol 5 forms 1D chains, in which the individual molecules are linked by hy-



Figure 2. Perspective view of the inclusion complex $5 \cdot bpy \cdot 0.5H_2O$.

Table 2. H	ydrogen-bond	parameters	[Å, °	of 5.b	oy•0.5H ₂ O

О–Н•••А	O–H	Н•••А	O…A	О–Н•••А
01–H1…N1	0.75(3)	2.02(3)	2.761(8)	176(3)
O2–H2···O7	0.80(4)	2.01(4)	2.779(7)	164(3)
O3–H3····O4	0.72(5)	2.05(5)	2.764(4)	172(5)
O4–H4…N3	0.82(4)	1.95(4)	2.767(8)	177(3)
O5-H5…N4	0.77(5)	2.09(5)	2.859(8)	171(5)
O6-H6···O1	0.69(3)	2.16(3)	2.842(4)	173(4)
O7–H7A…N2	0.96(7)	1.87(7)	2.796(8)	162(6)
O7–H7B…O5	0.79(4)	2.13(4)	2.91(1)	168(3)

drogen bridges (O2–H2···O1) and the phenyl rings are coplanar. The bpe molecules are situated approximately perpendicular to the 1D chains to which they are associated

Table 3. Hydrogen-bond parameters [Å, °] of 5. bpe.

•	• •			
О–Н•••А	O–H	Н•••А	O····A	О–Н•••А
01–H1····N2 02–H2···O3 03–H3····N1	0.82(3) 0.73(4) 0.76(5)	1.90(3) 2.03(4) 2.00(4)	2.716(5) 2.752(4) 2.755(5)	176(3) 171(4) 175(5)



Figure 3. Perspective view of the inclusion complex 5-bpe (only half of the outer bpe molecules are shown for clarity).



Figure 4. Perspective view of the inclusion complex 5. azpy.

Table 4. Hydrogen-bond parameters [Å, °] of 5·azpy.

О–Н•••А	O–H	Н…А	O…A	O–H···A
01–H1···O3	0.87(4)	1.91(4)	2.765(9)	165(4)
O2–H2…N3	0.84(4)	1.96(5)	2.783(4)	167(4)
O3–H3…N1	0.67(5)	2.15(5)	2.817(5)	176(6)
O4–H4…N4	0.71(5)	2.16(5)	2.866(4)	175(5)
O5–H5…N2	0.61(4)	2.24(4)	2.832(4)	169(4)
O6–H6····O4	0.64(4)	2.19(4)	2.81(1)	164(5)

through hydrogen bonding (O1-H1···N2/O3-H3···N1). The almost square-like voids defined by this 2D brick-wall net-

Table 5.	Hydrogen-bond	parameters	[Å, °] of 5.bpa.
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О–Н•••А	O–H	Н…А	O…A	О–Н•••А
01–H1···N1	0.67(5)	2.20(5)	2.871(7)	171(5)
02–H2···N2	0.78(5)	2.07(5)	2.828(6)	166(5)
03–H3···O2	0.85(5)	1.95(5)	2.782(7)	165(4)



Figure 5. Perspective view of the inclusion complex 5. bpa.

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work are approximately 10×10 Å and blocked mostly by trisilanol molecules of adjacent layers running parallel.

A perspective view of the inclusion complex 5. azpy is shown in Figure 4. Hydrogen-bond parameters are collected in Table 4. The asymmetric unit contains two crystallographically independent molecules of 5 (denoted as A and B) and azpy. All hydrogen atoms related to hydrogen bonds have been located during the X-ray data refinement. Similar as observed for the two previous structures, the trisilanol molecules are associated through hydrogen bonds (O1-H1...O3/O6-H6...O4) and give rise to the formation of 1D chains. However, unlike the two previous structures, the phenyl rings are not coplanar. The overall supramolecular motif may be also described as 2D brick-wall structure. The azpy pillars occur pair-wise and are situated approximately perpendicular to the 1D chains to which they are associated through hydrogen bonds (O2-H2···N3/O3-H3···N1/O4-H4…N4/O5-H5…N2). The almost square-like voids defined by the supramolecular arrangement are approximately 16×16 Å and filled by the same interpenetrating 2D brickwall network. To the best of our knowledge interpenetrating networks^[14] have not vet been observed for silanol structures.[1]

A perspective view of the inclusion complex 5·bpa is shown in Figure 5. Hydrogen-bond parameters are collected in Table 5. The asymmetric unit contains one molecule of 5 and bpa. All hydrogen atoms associated with hydrogen bonding have been located during the refinement. As observed in the structures before, the trisilanol molecules are associated through hydrogen bonds (O3–H3···O2) giving rise to the formation of 1D chains, in which the phenyl groups are not coplanar. The bpa pillars are situated approximately perpendicular to the 1D chains to which they are associated through hydrogen bonding (O1–H1···N1/O2– H2···N2). The almost square-like voids defined by the supramolecular pattern are approximately 8×8 Å.

The close examination of hydrogen-bond parameters (Tables 1–5) reveals no significant difference between O–H···O(H)Si and O–H···N hydrogen bonds. The donor–acceptor distances of the hydrogen bridges of all four structures range from 2.684(3) to 2.91(1) Å with an average of 2.78(1) Å and compare well with previously reported experimental values^[1–5] as well as parameters established computationally in the gas phase for H₃SiOH···O(H)SiH₃ (2.863 Å) and H₃SiOH···pyridine (2.815 Å) at the B3LYP/ 6-311+(2d,p) level of theory.^[15]

Applications in supramolecular chemistry and crystal engineering require that the molecular building blocks are rigid and that the functional groups possess a pre-fixed directionality.^[7] In an effort to qualitatively examine the conformational flexibility of the silanols groups, the O–Si–C–C torsion angles have been assessed and compared for all structures. The absolute torsion angles can vary between 2.5(2) and 70.3(2)°; however, most values are close to the average of $25.5(2)^{\circ}$ for all structures. The average of these values for each individual trisilanol molecule varies only between 20.6(2) and $31.4(2)^{\circ}$, which apparently suggests that the silanol groups cannot adopt conformations that are en-

tirely independent from the influence of the other two silanol groups attached to the same phenyl ring.

Conclusions

Regardless of the stoichiometric ratio of the reactants applied, the inclusion complexes between 5 and 4,4'-bis(pyridines), namely 5.bpy.0.5H2O, 5.bpe and 5.azpy, contain the same number of donor and acceptor molecules, which are associated by hydrogen bonding. The thermodynamic driving force of the co-crystallisation is the energy gain associated with the formation of O-H···N hydrogen bonds. This energy gain needs to be higher than that of the competitive O-H···O(H)Si hydrogen bonds. We have recently shown that the BSSE-corrected hydrogen-bond energies of the model compounds H₃SiOH···O(H)SiH₃ and H₃SiOH··· pyridine are -3.47 and -6.47 kcalmol⁻¹, respectively, at the B3LYP/6-311+(2d,p) level of theory.^[15] These values suggest that the highest energy gain should be observed when the ratio between trisilanol and 4,4'-bis(pyridine) is 2:3, allowing a maximum of three O-H···N hydrogen bridges. However, the loss of symmetry in a 2:3 complex and the associated increase of entropy, apparently, cannot be compensated entirely by the O-H···N hydrogen-bond energy. The formation of 1:1 complexes might be a compromise between the gain of hydrogen-bond energy and the loss of symmetry.

One of the more ambitious goals in supramolecular chemistry is the prediction of solid-state architectures.^[6] Interestingly, the crude supramolecular motifs are very similar for 5.bpy.0.5H₂O, 5.bpe and 5.azpy. In all three structures, the trisilanol molecules form 1D chains, which are interconnected by nearly perpendicular 4,4'-bis(pyridine) pillars to give rise to formation of 2D grid networks. However, the inevitable voids between the 2D grids differ substantially in size and shape for all four structures. The small voids of 5 \cdot bpa (8 \times 8 Å) are unfilled, the medium-sized voids of 5·bpy·0.5H₂O (10×12 Å) and 5·bpe (10×10 Å) are blocked by trisilanol molecules of adjacent 2D networks, whereas the larger voids of 5 azpy $(16 \times 16 \text{ Å})$ are filled by interpenetration. It might be interesting to see if these voids can be also filled with guest molecules that may possibly interact with the C-C and N-N double bonds of the bpe and azpy pillars.

Experimental Section

General: 1,3,5-Tribromobenzene, chlorodiisopropylsilane, 4,4'-bipyridine (bpy) and (*E*)-bis(4-pyridyl)ethylene (bpe) are commercially available, whereas 4,4'-azopyridine (azpy) and bis(4-pyridyl)acetylene (bpa) have been prepared according to known routes.^[16] NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and are referenced against Me₄Si. IR spectra were recorded with a 5 SXC Nicolet DTGS FT-IR spectrometer. Microanalyses were obtained with a Vario EL elemental analyser.

1,3,5-Tris(diisopropylsilyl)benzene (6): A 250-mL three-neck flask equipped with a septum, dropping funnel and reflux condenser was

charged with Mg turnings (4.75 g, 195 mmol), iPr₂SiHCl (24.0 g, 159 mmol) and THF (100 mL). The Mg was activated by addition of 1,2-dibromoethane (250 µL) through a syringe. 1,3,5-Tribromobenzene (15.3 g, 49.0 mmol) dissolved in THF (100 mL) was slowly added. The temperature was maintained at 40 °C for 12 h, before the mixture was hydrolysed by the addition of H₂O (50 mL). The organic layer was washed with water (3×20 mL) and dried with Na₂SO₄. Removal of the solvent and fractional distillation of the crude product in vacuo afforded 6 as an almost colourless viscous oil [11.5 g, 27.3 mmol (56%); b.p. 200–220 °C/7.5 10⁻³ Torr]. ¹H NMR (CDCl₃, 399.65 MHz): δ = 7.56 (s, 3 H, Ph), 3.86 [s, ¹J(¹H- 29 Si) = 182 Hz, 3 H, SiH], 1.16 (m, 6 H, CHMe₂), 0.98, 0.90 (d, 36 H, CHMe₂) ppm. ¹³C{¹H} NMR (CDCl₃, 100.40 MHz): δ = 143.4, 131.8 (Ph), 18.7, 18.4 (CHMe₂), 10.8 (CHMe₂) ppm. ²⁹Si{¹H} NMR (CDCl₃, 79.30 MHz): $\delta = 5.3$ [s, ${}^{1}J({}^{29}\text{Si}{}^{-1}\text{H}) = 184$ Hz] ppm. IR (KBr plates): $\tilde{v} = 2101$ (SiH) cm⁻¹. C₂₄H₄₈Si₃ (420.52): calcd. C 68.55, H 11.41; found C 68.53, H 11.45.

1,3,5-Tris(chlorodiisopropylsilyl)benzene (7): A 50-mL Schlenk flask with gas outlet was charged with **6** (10.5 g, 25 mmol) and sealed with a septum. An excess of SO₂Cl₂ (7 mL, 93 mmol) was slowly added through a syringe. After a short induction delay, a strongly exothermic reaction occurred and SO₂ gas vigorously evolved. During the reaction, the mixture was cooled with an ice bath. After the addition was complete, the mixture was stirred at room temperature for 24 h and at 40 °C for 1 h. Unreacted SO₂Cl₂ was removed in vacuo and the remaining crude product was purified by kugelrohr distillation to give **7** as a colourless low-melting solid [9.37 g, 17.9 mmol (72%); b.p. 220–240 °C/7.5 10⁻³ Torr]. ¹H NMR (CDCl₃, 399.65 MHz): δ = 7.89 (s, 3 H, Ph), 1.45 (m, 6 H, C*H*Me₂),

1.09, 1.01 (d, 36 H, CH*Me*₂) ppm. ¹³C{¹H} NMR (CDCl₃, 100.40 MHz): δ = 141.6, 130.7 (Ph), 16.9, 16.7 (*C*HMe₂), 13.7 (CH*Me*₂) ppm. ²⁹Si{¹H} NMR (CDCl₃, 79.30 MHz): δ = 26.4 (s) ppm. C₂₄H₄₅Cl₃Si₃ (523.87): calcd. C 54.99, H 8.65; found C 54.90, H 9.03.

1,3,5-Tris(hydroxydiisopropylsilyl)benzene (5): Compound 7 (8.23 g, 16 mmol) dissolved in diethyl ether (40 mL) was treated with an aqueous solution (40 mL) of NaOH (5.28 g, 132 mmol). The mixture was stirred at room temperature for 3 h before the layers were separated. The organic layer was washed with H₂O (3×40 mL) and dried with Na₂SO₄. The removal of the solvent in vacuo produced a colourless solid that was recrystallised from CH2Cl2/hexane to furnish 5 as colourless crystals [3.2 g, 6.8 mmol (43%); m.p. 90-91 °C]. ¹H NMR (CDCl₃, 399.65 MHz): δ = 7.74 (s, 3 H, Ph), 2.39 (s, OH), 1.20 (m, 6 H, CHMe₂), 1.00, 0.92 (d, 36 H, CHMe₂) ppm. ¹³C{¹H} NMR (CDCl₃, 100.40 MHz): δ = 140.7, 132.7 (Ph), 17.1, 16.9 (CHMe₂), 12.4 (CHMe₂) ppm. ²⁹Si{¹H} NMR (CDCl₃, 79.30 MHz): δ = 7.0 (s) ppm. IR (KBr pellet): \tilde{v} = = 3694, 3345 (OH) cm⁻¹. C₂₄H₄₈O₃Si₃ (468.89): calcd. C 61.48, H 10.32; found C 61.53, H 10.62. Slow recrystallisation from toluene afforded 5.0.5H2O. C48H98Si6O7 (955.80): calcd. C 61.32, H 10.33; found C 60.13, H 10.50.

Synthesis of the Inclusion Complexes of 5 with 4,4'-Bis(pyridines): Compound 5 (50 mg, 0.107 mmol) and the appropriate amount of the 4,4'-bis(pyridines) (byp: 10.7 mg, bpe: 13.0 mg, azpy: 13.7 mg, 0.070 mmol) were dissolved in CH₂Cl₂/hexane (3:2). Slow concentration of the solution furnished colourless or orange crystals. The yields were not optimised. **5**·byp·0.5H₂O: Yield 20 mg (30%). C₆₈H₁₁₃N₄O₇Si₆ (1267.19): calcd. C 64.40, H 9.06, N 4.42; found

Table 6. Crystal data and structure refinement of 5.0.5H2O, 5.bpy.0.5H2O, 5.bpe, 5.azpy and 5.bpa.

	5 •0.5H ₂ O	5 •bpy•0.5H ₂ O	5.bpe	5·azpy	5·bpa
Empirical formula	C48H90O7Si6	C ₆₈ H ₁₁₃ N ₄ O ₇ Si ₆	C ₃₆ H ₅₈ N ₂ O ₃ Si ₃	C34H56N4O3Si3	C ₃₆ H ₅₆ N ₂ O ₃ Si ₃
Formula mass [gmol ⁻¹]	947.75	1267.18	651.11	653.10	649.10
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Crystal size [mm]	$0.60 \times 0.63 \times 0.83$	$0.11 \times 0.22 \times 0.42$	$0.01 \times 0.15 \times 0.05$	$0.02 \times 0.14 \times 0.50$	$0.05 \times 0.07 \times 0.37$
Space group	C2/c	ΡĪ	$P2_1/c$	Pn	C2/c
a [Å]	17.910(2)	11.068(3)	10.763(2)	17.054(4)	34.326(9)
b [Å]	43.010(6)	16.077(4)	23.687(5)	11.947(3)	11.798(3)
c [Å]	23.406(3)	22.753(5)	16.169(4)	20.495(5)	21.652(5)
a [°]	90	103.633(6)	90	90	90
β[°]	94.643(4)	98.387(5)	108.016(5)	110.609(5)	117.209(7)
γ [°]	90	101.752(5)	90	90	90
V [Å ³]	17970(4)	3771.2(15)	3920.1(15)	3908.5(15)	7798(3)
Z	12	2	4	4	8
$\rho_{\rm calcd.} [{\rm Mg} \cdot {\rm m}^{-3}]$	1.051	1.116	1.103	1.110	1.106
<i>T</i> [K]	143	133	173	173	173
μ (Mo- K_{α}) [mm ⁻¹]	0.180	0.160	0.155	0.157	0.155
F(000)	6216	1378	1416	1416	2816
θ range [°]	0.95 to 25.00	0.94 to 25.00	1.58 to 25.00	1.34 to 25.00	0.98 to 25.00
Index ranges	$-16 \le h \le 21$	$-13 \le h \le 13$	$-12 \le h \le 11$	$-12 \le h \le 11$	$-17 \le h \le 40$
	$-51 \le k \le 51$	$-17 \le k \le 19$	$-28 \le k \le 28$	$-28 \le k \le 28$	$-14 \le k \le 13$
	$-27 \le l \le 15$	$-22 \le l \le 27$	$-19 \le l \le 19$	$-19 \le l \le 19$	$-24 \le l \le 25$
No. of reflections collected	44816	25707	31128	23848	16008
Completeness to θ_{max}	99.3%	97.6%	99.9%	99.6%	98.0%
No. independent reflections	15720	12955	6905	10302	6736
No. obsd. reflns. with	11206	0210	4700	0007	2640
$[I > 2\sigma(I)]$	11090	9210	4/99	9097	2049
No. refined parameters	835	798	409	817	409
$GooF(F^2)$	1.010	1.035	1.069	1.103	0.876
$R_1(F) [I \ge 2\sigma(I)]$	0.048	0.050	0.0519	0.0366	0.0660
$wR_2(F^2)$ (all data)	0.151	0.140	0.1561	0.1042	0.1980
$(\Delta/\sigma)_{\rm max}$	0.002	0.002	0.001	0.002	0.001
Largest diff peak/hole [e·Å-3]	2.498/-0.391	0.768/-0.253	0.546/-0.363	0.376/-0.217	0.374/-0.380

FULL PAPER

C 63.78, H 9.40, N 4.06. **5·bpe:** Yield 30 mg (43%). $C_{36}H_{58}N_2O_3Si_3$ (651.13): calcd. C 66.41, H 8.98, N 4.30; found C 66.35, H 9.19, N 4.27. **5·azpy:** Yield 40 mg (57%). $C_{34}H_{56}N_4O_3Si_3$ (653.09): calcd. C 62.53, H 8.64, N 8.58; found C 62.31, H 8.58, N 8.44. **5·bpa:** Yield 40 mg (57%). $C_{36}H_{56}Si_3N_2O_3$ (648.10): calcd. C 66.61, H 8.70, N 4.32; found C 66.12, H 8.71, N 4.19.

X-ray Crystallography: Intensity data were collected with a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo- K_{α} (0.7107 Å) radiation. Data were reduced using the program SAINT.^[17] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.^[18] Full-matrix least-squares refinements on F^2 , using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Disorder of an isopropyl group in 5.0.5H₂O was resolved with split occupancies of 0.6 and 0.4 for C81 and C81'. The large residual electron density (2.498 e·Å⁻³) might be indicative for disorder (of O12) or an unaccounted solvent molecule; however, all attempts of modelling failed. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Hydrogen atoms attached to oxygen atoms were located from the electron-density maps of 5.bpy.0.5H2O, 5.bpe, 5.azpy and 5.bpa and refined isotropically without restraints. The absolute configuration of 5-azpy has been determined by the refinement of the Flack parameter [0.00(8)]. Figures were created using DIAMOND.^[19] Further details are listed in Table 6. CCDC-605353 (5.0.5H₂O), -605354 (5.bpy.0.5H₂O), -605355 (5.bpe), -605356 (5·azpy) and -605357 (5·bpa) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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